

Interactive comment on “Size and composition measurements of background aerosol and newparticle growth in a Finnish forest during QUEST 2 using an Aerodyne Aerosol Mass Spectrometer” by J. D. Allan et al.

J. D. Allan et al.

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I think the AMS wire data and related discussions are not directly relevant to the main findings/points presented in this paper... Authors' response: While the wire data does not directly relate to the scientific conclusions of this paper, it does partly address some of the quantification issues that were raised in previous publications and conferences, which are important to deal with from a quality assurance point of view. The implications of the figure should perhaps have been explained in greater detail. While the figure shows that the beam is divergent to an extent, we can only make a proper as-

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assessment of whether it is affecting the data when it is compared with the modelling work of Huffman et al. (AS&T, in press). The relative attenuation at the centre wire position is approximately 30 %, although this will be a low estimate if the leftmost point is disregarded. On the other hand, the model shows that if the beam were to divergent enough to be responsible for a significant amount of particle loss, the centre attenuation would be less than around 15 %, i.e. more of the detected particle beam would be contained in the other wire positions. The data in this paper shows that the concerns about beam divergence raised previously are not affecting the data in this instance, although the problem of bounce is an entirely separate issue which cannot be dealt with here, so will be the subject of future publications. The text has been amended to explain this.

A main focus of the paper is to investigate the roles played by organic compounds in new particle growth and the compounds that were possibly involved... Authors' response: The organic m/z scanned were 27, 43, 44, 55, 57, 67, 77 and 91, although not all of these yielded satisfactory signals. These are listed in the revised text. Also included are extra traces accompanying figure 9 that show the size-resolved signals of the fragments. A comparison of event/non-event mass spectra would be desirable, but unfortunately there were no non-event days recorded by the AMS during the campaign that were not possibly influenced by continental air (as shown by back trajectories), so a meaningful comparison is not possible.

It also puzzles me why standard EI mass spectrum, rather than AMS spectrum, of verbenone is presented, especially since the two spectra are likely to be very different? In terms of presentation, it will be helpful that minor tick markers (better of 1 unit m/z increment) are shown in the mass spectra (Figs. 4, 8, 10). Authors' response: While the NIST library spectra tend to be different to the AMS, this tends to only be in the relative sizes of the peaks and a general bias towards the higher mass units. Laboratory studies have shown that the m/z locations of the peaks are conserved, which is what the figure is seeking to illustrate. Extra ticks have been added as suggested.

In addition, I think it is worthwhile to demonstrate the correlation between the DMPS and AMS size distributions in Figs 6 and 7 by 1) including the DMPS particle volume (or mass) image plots and 2) scaling the y axes of the image plots by assumed particle density so that D_{va} is related to D_m . Authors' response: Volume distributions were originally not included in this manuscript due to the fact that the ambient accumulation mode distracts from the Aitken mode due to the lack of chemical speciation. However, at the request of both reviewers, they have been included in the resubmission. Volume has been used as we are unwilling to assume a density of the particles. The lack of signal-to-noise prevents the derivation of this parameter, as has been performed during other field measurements.

Page 8758, line 4, remove “the” in front of “each”. Authors' response: Corrected.

Page 8758, line 25, change “they” into “the”. Authors' response: Corrected.

Page 8759, 2nd sentence, to my knowledge, Zhang et al. (ES&T, 2004) reported that the composition of the growing particles was predominantly ammonium sulfate... Authors' response: While this is true, the period of interest in this study is the earliest stages of growth observable, which is sulphuric acid in the Zhang et al. study, which is in contrast to this study. The referring text has been modified to stress this.

Page 8759, line 24, remove “has” in front of “was”. Authors' response: Corrected.

Page 8761, 3rd sentence of the 3rd paragraph, I don't think that “the AMS data provide the direct linkage between data from the sizing instrument and the chemical information from offline analyses”... Authors' response: The advantage of the AMS is that thanks to its greater size and time resolutions, it makes linking the DMPS number distributions to the chemical compositions much easier. However, it is agreed that the term ‘direct’ in this context is a little strong; this has been reworded in the text as follows; “..reduce the ambiguity when linking..”

Page 8761, line 29, please consider revising “Particles less than the lower limit”. Au-

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thors' response: Reworded as; "Particles smaller than 30 nm"

Page 8764, last sentence of 1st paragraph: please specify the RH ranges corresponding to collection efficiencies of 0.5 and 1, respectively. Authors' response: As discussed in a previous paper (Allan et al. 2004b), the ambient aerosol tends to be at a low RH at the point of entry into the instrument due to a combination of the temperature difference between ambient and cabin and conductive heating from the instrument's body. As a result, in almost all external comparisons performed when no temperature control was used, the collection efficiency was measured as 0.5. This is explained more clearly in the text.

Page 8766, line 7, insert Dva in front of <200nm. Authors' response: Corrected.

Page 8766, a side-by-side mass spectra comparison of organics during non-event vs. event days will be helpful. Authors' response: See response to comment above. However, a mass spectrum from continental-influenced air has been included in figure 8 to act as a point of reference.

Page 8768, line 8-10, I'd like to point out that the oxygenated organic signal at m/z 30 (CH₂O⁺) may not necessarily be a small feature in mass spectra of ambient or lab organic aerosols. Authors' response: The term 'small' should perhaps have been qualified a little better. While a peak at this m/z is certainly possible, there has been no oxygenated species tested in the laboratory where the peak at m/z 30 has been the base peak or has even approached the size of the base peak. Given that the peak at m/z 30 was frequently found to be of a similar size at m/z 43 during this study (and, more to the point, much greater than m/z 29, which is generally a larger peak than 30 in oxygenated spectra, even for molecular formaldehyde), this would be a requirement for any candidate species or family. The text has been reworded to make this clearer.

Page 8769, lines 8 and 9, I have trouble understanding "the instrument response is largely invariant at alkane C # > 10". Is it according to the appearance of the mass spectra? Authors' response: This should have been made clearer. The invariance is

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in the m/z of the base peak and the relative sizes of the other peaks to the base. The absolute instrument response is linear with mass, as with all species detected. The text has been reworded to this effect.

Page 8770, lines 10- 12, please clarify “the relatively abundances of carbon, hydrogen, and oxygen are conserved in the fragments”. I also have trouble understanding why “the low m/z peaks could be indicative of terpene oxidation products”? Please clarify. Authors’ response: The term ‘low m/z peaks’ should really be stated to be low relative to the adjacent peaks in the alkane series. This can happen, as is explained earlier in the text, if the ratio of carbon to hydrogen is high (due to cyclic or unsaturated features) or the presence of oxygen atoms in these fragments. This will still apply even if the molecule has undergone additional thermal fragmentation, as the elemental ratios will be conserved. The text has been reworded to make this clearer.

Page 8770, 2nd paragraph, another possible reason for the lack of organic mass in particles $< 200\text{nm}$ at low concentrations of monoterpene oxidation products... Authors’ response: Agreed that this is certainly plausible but there are too many uncertainties that would need to be taken into account to make a systematic comparison a useful exercise from the point of view of this paper. Most important is the fact that the species detected in the gas phase are by no means the same as those in the particle phase, as additional reactions may be required as part of the condensation process, which would in turn mean that the available surface area may not be the determining factor in the conversion between phases. Also, even if a relationship is found, it will be difficult to separate the conclusion that the accumulation mode is acting as a sink of gas-phase terpene oxidation products from changes in the source footprint being responsible, which is likely to be a major (but difficult to quantify) factor. The concluding remark of the paragraph has been reworded, qualifying the absent organic particulate matter as being ‘Aitken mode’. This statement, while not dealing with the issue of an accumulation mode sink explicitly, is not affected by it. The exact loss mechanisms of the gas phase species is a much larger issue and is considered outside the scope of

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this paper.

Page 8772, please revise the first sentence of the 2nd paragraph. To my knowledge, the organic AMS signature during event days presented in this study has been observed in several rural/remote locations. These results have been presented at conferences although I am not aware of the publication of similar results. Authors' response: The reviewer is indeed correct, although these were brought to our attention during conferences that took place after this paper was initially submitted. Some of these results are in part due to a refinement of the techniques used to separate the different components of the organic spectra, which has allowed candidate biogenic SOA spectra to be extracted free from interferences from other sources. However, this work is very much ongoing and no submissions to the peer-reviewed literature currently are planned (to our knowledge). The text has been revised and references inserted.

Page 8780, Fig 1, please define the x axis. What are the "sectors" corresponding to? I'd like to suggest the use of more viable units (such the ratio of the distance from the edge/center of the vaporizer to the diameter of the vaporizer), rather than arbitrary units. Authors' response: The graph has been modified as suggested, so the position is now ratio to the edge of the vaporiser.

Page 8784, I think it will be helpful to show the side-by-side average AMS size distributions during event and non-event days as well. Authors' response: See above. This is more or less covered by figures 2 and 3.

Pages 8785-8786, Figs 6 & 7, why are the images so pixilated? If any averaging is applied to the AMS data, please mention it in the text and/or in the captions. Authors' response: Averaging has indeed been performed on the AMS data for the sake of clarity, as the raw data is far too noisy to be used in this type of plot. This note has been added to the text.

Page 8786, please define the parameter that is plotted in Fig. 7a, is it total organic mass or total mass? Authors' response: It is total organic mass. The caption has been

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modified to make this more explicit.

Page 8787, caption of Fig. 8, the use of “sources” here is rather vague. Authors’ response: Reworded as “contributions from other known atmospheric organic species.”

Page 8788, 2nd sentence of the caption of Fig. 9, check subject and verb agreement. Authors’ response: Corrected

Page 8789, fig. 10, while it is true that the high temperature evaporation process of organic compounds in the AMS... Authors’ response: Unfortunately, while an AMS mass spectrum of verbenone is desirable, it is currently unobtainable due to a lack of instrument availability (all our AMS units are tied up with fieldwork commitments for the coming months), so will have to be a feature in a future publication. While aromatics give very high m/z peaks in the AMS, this is specifically due to the high fragmentation energy and stability of the benzene ring structure, which verbenone does not possess. These points are addressed in the revised text.

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